

In-gap Bound States Induced by Interstitial Fe Impurities in Iron-based Superconductors

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Based on a two-orbit four-band tight binding model, we investigate the low-lying electronic states around the interstitial excess Fe ions in the iron-based superconductors by using T-matrix approach. It is shown that the local density of states at the interstitial Fe impurity (IFI) possesses a strong resonance inside the gap, which seems to be insensitive to the doping and the pairing symmetry in the Fe-Fe plane, while a single or two resonances appear at the nearest neighboring (NN) Fe sites. The location and height of the resonance peaks only depend on the hopping t and the pairing parameter Δ_I between the IFI and the NN Fe sites. These in-gap resonances are originated in the Andreev's bound states due to the quasiparticle tunneling through the IFI, leading to the change of the magnitude of the superconducting order parameter. When both t and Δ_I are small, this robust zero-energy bound state near the IFI is consistent with recent scanning tunneling microscopy observations.

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The discovery of different families of the iron-based superconductors provided us a new platform to study high temperature superconductivity [1-6]. It has been reported that the superconducting transition temperature T_c can reach as high as 55K [2]. Similar to the cuprate superconductors, the iron-based superconductors also have a layer structure and the superconductivity comes from the Cooper pairs in the Fe-Fe plane by doping electrons or holes. However, different from the oxygen ions at the Cu-Cu bonds in the cuprates, two As/Se/Te ions in each unit cell locate just above (below) the center of one face of the Fe square lattice and below (above) the center of the neighboring face, respectively (see Fig. 1). Such a combination of the Fe ions and the As/Se/Te ions produces a more complex energy band structure. Angle resolved photoemission spectroscopy (ARPES) experiments have revealed that the iron-based superconductors usually possess two hole Fermi surfaces around (0,0), i.e. Γ point, and two electron Fermi surfaces around (π, π) , i.e. M point [7-16]. We note that due to different dopings, one or even two hole Fermi surfaces disappear in some families of the iron-based superconductors. In order to explain these Fermi surface characteristics, two-orbital, three-orbital, and five-orbital tight binding models have been proposed [17-20].

It is known that the impurity effects play a crucial role in exploring superconductivity [21]. The strong zero-energy bound state (ZBS) at the Zn ion and the fourfold symmetric electronic states around the single impurity, observed by scanning tunneling microscopy (STM) [22], demonstrate that the superconducting order parameter in the cuprates has a d-wave symmetry. The in-gap resonances induced by a nonmagnetic impurity was also used to confirm the s_{+-} pairing symmetry in the iron-based superconductors [18]. It is clear that these resonance peaks are originated in the Andreev's bound states due

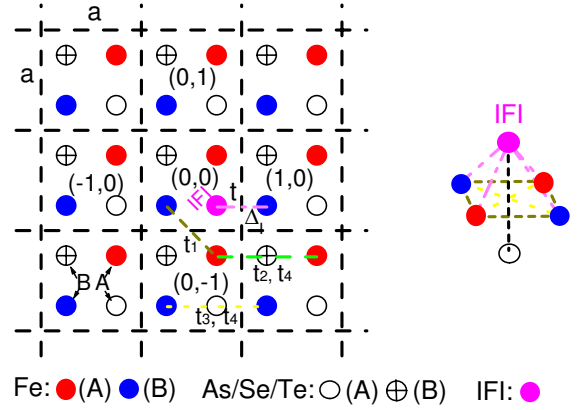


FIG. 1: (Color online) Schematic lattice structure of the Fe-As/Se/Te layers with each unit cell containing two Fe (A and B) and two As/Se/Te (A and B) ions. The As/Se/Te ions A and B are located just below and above the center of each face of the Fe square lattice, respectively. Here, t_1 is the nearest neighboring (NN) hopping between the same orbitals d_{xz} or d_{yz} . t_2 and t_3 are the next nearest neighboring hoppings between the same orbitals mediated by the As/Se/Te ions B and A, respectively. t_4 is the next nearest neighboring hopping between the different orbitals. The IFI is situated at the symmetric position of As/Se/Te ion about the Fe-Fe plane. t and Δ_I are the hopping and the pairing parameters between the same orbitals of the IFI and the NN Fe sites, respectively.

to the quasiparticle scattering between the Fermi surfaces or parts of the Fermi surface with opposite phases of the superconducting order parameter.

Very recently, Yin *et al.* also used STM to study the electronic states near the interstitial excess Fe ions in the iron-based superconductor Fe(Te,Se) [23]. The as-grown Fe(Te,Se) single crystals usually contain a large amount of excess Fe ions situated randomly at the interstitial

sites, which are the symmetric points of the Te/Se ions about the Fe-Fe plane (see Fig. 1). They found that the differential conductance at the interstitial Fe impurity (IFI) also has a strong ZBS. The height of this resonance decays rapidly with the distance from the IFI and vanishes at about 10 Å. It is especially surprising that the ZBS at the IFI is not affected by a magnetic field up to 8 Tesla. Such a ZBS induced by out of the superconducting plane impurities was never reported before, and its origin is unclear up to now.

In this work, we provide an explanation for the interesting observation of the robust ZBS. Because the big family of the iron-based superconductors has a similar energy band structure, here we employ the two-orbit four-band tight binding model presented in Ref. [18] to explore the origin of the ZBS near the IFI. We remember that this energy band structure was constructed by starting two degenerate orbitals d_{xz} and d_{yz} of per Fe ion and two Fe ions in each unit cell, and fitted well the ARPES observations. Because the asymmetry of the above and below As/Se/Te ions in the Fe-As/Se/Te surface layer was taken into account, the model naturally explained several important STM observations, e.g. in-gap impurity resonances [18,24], the bound state at negative energy in the vortex core [25,26], the domain walls [27-30], etc., and especially repeated the phase diagram measured by nuclear magnetic resonance and neutron scattering experiments [31-33].

It is obvious that the IFI is different from the nonmagnetic, magnetic, and Kondo impurities in the superconducting plane. Because Fe ion is assumed to possess two electron channels, the electrons in the Fe-Fe plane can tunnel through the IFI. Now we know that superconductivity in the iron-based superconductors originates from electron pairing between the next nearest neighboring Fe sites. So only one electron of a Cooper pair can arrive at the IFI in the superconducting state. Therefore, the Hamiltonian describing the IFI in the iron-based superconductors has the form

$$H = H_0 + H_{\text{BCS}}$$

$$\begin{aligned} & -t \sum_{\alpha\sigma} \{c_{\alpha\sigma}^+ [c_{A\alpha,00\sigma} + c_{B\alpha,00\sigma} + c_{A\alpha,0-1\sigma} + c_{B\alpha,10\sigma}] + \text{h.c.}\} \\ & + \Delta_I \sum_{\alpha} \{c_{\alpha\uparrow}^+ [c_{A\alpha,00\downarrow}^+ + c_{A\alpha,0-1\downarrow}^+ + c_{B\alpha,00\downarrow}^+ + c_{B\alpha,10\downarrow}^+] \\ & + c_{\alpha\downarrow}^+ [c_{A\alpha,00\uparrow}^+ + c_{A\alpha,0-1\uparrow}^+ + c_{B\alpha,00\uparrow}^+ + c_{B\alpha,10\uparrow}^+] + \text{h.c.}\}, \quad (1) \end{aligned}$$

where H_0 is the two-orbit four-band tight binding model proposed in Ref. [18], H_{BCS} is the mean field BCS pairing Hamiltonian in the Fe-Fe plane, $c_{A(B)\alpha,ij\sigma}^+$ ($c_{A(B)\alpha,ij\sigma}$) creates (destroys) an α electron with spin σ ($=\uparrow$ or \downarrow)

in the unit cell $\{i, j\}$ of the sublattice A (B), $\alpha = 0(1)$ represents the degenerate orbital d_{xz} (d_{yz}), and t and Δ_I are the hopping and pairing parameters between the same orbitals of the IFI and the nearest neighboring (NN) Fe sites, respectively.

We note that the sub-Hamiltonian $H_0 + H_{\text{BCS}}$ can be diagonalized by suitable transformations. Introducing first the Fourier transformation $c_{A(B)\alpha,ij\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} c_{A(B)\alpha,\mathbf{k}\sigma} e^{i(k_x x_i + k_y y_j)}$ with N the number of unit cells and the canonical transformations $c_{A\alpha,\mathbf{k}\sigma} = \sum_{uv} (-1)^{\alpha v} \frac{a_{u,\mathbf{k}}}{\Gamma_{u,\mathbf{k}}} \phi_{uv,\mathbf{k}\sigma}$ and $c_{B\alpha,\mathbf{k}\sigma} = \sum_{uv} (-1)^{\alpha v} \frac{\epsilon_{T,\mathbf{k}}^*}{\Gamma_{u,\mathbf{k}}} \phi_{uv,\mathbf{k}\sigma}$ with $u, v = 0$ and 1 , $a_{u,\mathbf{k}} = \frac{1}{2}(\epsilon_{A,\mathbf{k}} - \epsilon_{B,\mathbf{k}}) + (-1)^u \sqrt{\frac{1}{4}(\epsilon_{A,\mathbf{k}} - \epsilon_{B,\mathbf{k}})^2 + \epsilon_{T,\mathbf{k}} \epsilon_{T,\mathbf{k}}^*}$, $\epsilon_{A,\mathbf{k}} = -2(t_2 \cos k_x + t_3 \cos k_y)$, $\epsilon_{B,\mathbf{k}} = -2(t_2 \cos k_y + t_3 \cos k_x)$, $\epsilon_{T,\mathbf{k}} = -t_1[1 + e^{ik_x} + e^{ik_y} + e^{i(k_x+k_y)}]$, and $\Gamma_{u,\mathbf{k}} = \sqrt{2(a_{u,\mathbf{k}}^2 + \epsilon_{T,\mathbf{k}} \epsilon_{T,\mathbf{k}}^*)}$, and then taking the Bogoliubov transformations $\phi_{uv\mathbf{k}\uparrow} = \sum_{\nu=0,1} (-1)^\nu \xi_{uv\mathbf{k}\nu} \psi_{uv\mathbf{k}\nu}$ and $\phi_{uv\mathbf{k}\downarrow}^+ = \sum_{\nu=0,1} \xi_{uv\mathbf{k}1-\nu} \psi_{uv\mathbf{k}\nu}$ with constants $\xi_{uv\mathbf{k}\nu}$ to be determined below, the total Hamiltonian H finally becomes

$$\begin{aligned} H = & \sum_{uv\mathbf{k}\nu} (-1)^\nu \Omega_{uv\mathbf{k}} \psi_{uv\mathbf{k}\nu}^+ \psi_{uv\mathbf{k}\nu} \\ & + \frac{1}{\sqrt{N}} \sum_{uv\alpha\mathbf{k}\nu} (\mathcal{M}_{uv\mathbf{k}\nu,\alpha} c_{\alpha\uparrow}^+ \psi_{uv\mathbf{k}\nu} + \mathcal{N}_{uv\mathbf{k}\nu,\alpha} c_{\alpha\downarrow}^+ \psi_{uv\mathbf{k}\nu} + \text{h.c.}), \quad (2) \end{aligned}$$

where $\Omega_{uv\mathbf{k}} = \sqrt{(E_{uv\mathbf{k}} - \mu)^2 + \Delta_{uv\mathbf{k}}^2}$, $E_{uv\mathbf{k}} = \frac{1}{2}(\epsilon_{A,\mathbf{k}} + \epsilon_{B,\mathbf{k}}) - 2(-1)^v t_4 (\cos k_x + \cos k_y) + (-1)^u \sqrt{\frac{1}{4}(\epsilon_{A,\mathbf{k}} - \epsilon_{B,\mathbf{k}})^2 + \epsilon_{T,\mathbf{k}} \epsilon_{T,\mathbf{k}}^*}$, $\mathcal{M}_{uv\mathbf{k}\nu,\alpha} = (-1)^{\alpha v} \tau_{u,\mathbf{k}}^* [-(-1)^\nu t \xi_{uv\mathbf{k}\nu} + \Delta_I \xi_{uv\mathbf{k}1-\nu}]$, $\mathcal{N}_{uv\mathbf{k}\nu,\alpha} = (-1)^{\alpha v} \tau_{u,\mathbf{k}} [-t \xi_{uv\mathbf{k}1-\nu} + (-1)^\nu \Delta_I \xi_{uv\mathbf{k}\nu}]$, $\tau_{u,\mathbf{k}} = [(1 + e^{ik_y}) a_{u,\mathbf{k}} + (1 + e^{-ik_x}) \epsilon_{T,\mathbf{k}}] / \Gamma_{u,\mathbf{k}}$, $\xi_{uv\mathbf{k}0} \xi_{uv\mathbf{k}1} = \Delta_{uv\mathbf{k}} / (2\Omega_{uv\mathbf{k}})$, and $\xi_{uv\mathbf{k}\nu}^2 = \frac{1}{2} [1 + (-1)^\nu (E_{uv\mathbf{k}} - \mu) / \Omega_{uv\mathbf{k}}]$. Here, μ is the chemical potential to be determined by doping and $\Delta_{uv\mathbf{k}}$ is the superconducting order parameter in the Fe-Fe plane. We can see from the Hamiltonian (2) that the hopping t may form new electron-fermion pairs while the pairing parameter Δ_I can also induce a hopping term. In other words, new quasiparticles are excited if electrons tunnel through the IFI. It is expected that such a novel mechanism produces the ZBS observed by the STM [23].

The Hamiltonian H in Eq. (2) has a quadratic form of the fermionic operators and can be exactly solved by using the T-matrix approach [18,21]. The analytic expression of the LDOS near the IFI has been obtained at different bias voltages. In our calculations, we have used the energy band parameters: $t_1 = 0.5$, $t_2 = 0.2$, $t_3 = -1.0$, and $t_4 = 0.02$. We note that the iron-based superconductor Fe(Te,Se) in the STM experiment [23] has a small gap of about 1.5 meV. In order to clearly observe the change of the impurity resonance peaks with the bias

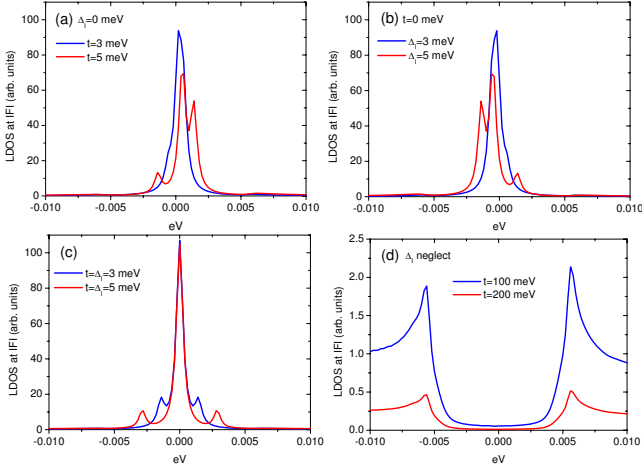


FIG. 2: (Color online) The LDOS at the IFI as a function of the bias voltage eV under different t and Δ_I for the s_{+-} pairing symmetry $\Delta_{uv\mathbf{k}} = \frac{1}{2}\Delta_0(\cos k_x + \cos k_y)$ with $\Delta_0 = 5.8$ meV at optimal electron doping ($\mu = -0.54$), where there are two Fermi surface sheets around Γ point.

voltage, here we employ a large gap, i.e. 5.8 meV, in the electron-doped $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ [34,35], where the excess Fe or Co ion is also regarded as an IFI. In Fig. 2, we plot the LDOS at the IFI as a function of the bias voltage eV under different t and Δ_I for the s_{+-} pairing symmetry at the chemical potential $\mu = -0.54$, where there are two Fermi surface sheets around the center of the Brillouin zone, i.e. Γ point. Obviously, when t or Δ_I is small, i.e. $< \sim 3$ meV, the LDOS has a strong resonance peak at zero energy, and the superconducting coherence peaks do not show up. With increasing t or Δ_I , the sharp zero energy resonance peak moves toward positive or negative energy, respectively, and the superconducting coherence peaks appear at the symmetric bias voltages in Fig. 2(a) and (b). The height of the coherence peak at the positive energy is higher (lower) than that at the negative energy for the parameter t (Δ_I). We note that when $t < \sim 4$ meV and $\Delta_I = 0$ meV, where the coherence peak at the negative energy disappears, the LDOS at the IFI has a single- or double-peak structure at the positive energies, very similar to the STM observations in the black regions of the superconducting $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ sample [35]. When $t = \Delta_I = 3$ and 5 meV, the LDOS possesses the strong ZBS and the symmetric coherence peaks, shown in Fig. 2(c). However, the superconducting energy gap at the IFI is smaller than in the bulk, i.e. $\Delta_0 = 5.8$ meV, and becomes larger if t or Δ_I increases. When t is large enough to neglect Δ_I , the superconducting energy gap at the IFI is equal to Δ_0 , and there is no in-gap bound state in Fig. 2(d).

Fig. 3 shows the LDOS at the NN Fe sites of the IFI for the s_{+-} pairing symmetry under $\mu = -0.54$. When $t(\Delta_I) \sim 2$ meV and $\Delta_I(t) = 0$ meV, there is a ZBS appeared in the LDOS (see Fig. 3(a) and (b)). With

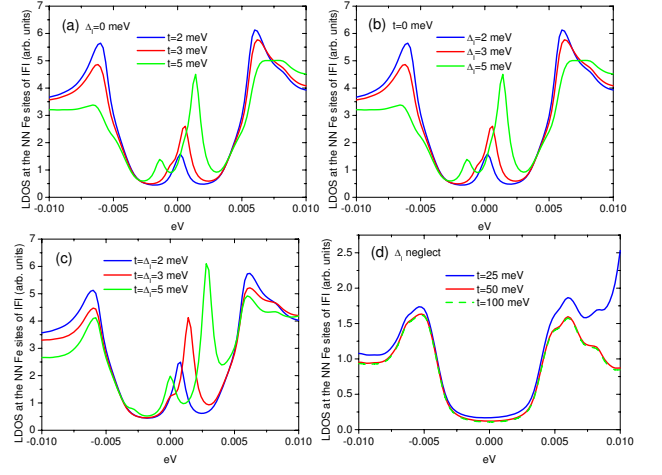


FIG. 3: (Color online) The LDOS at the nearest neighboring Fe sites as a function of the bias voltage eV under different t and Δ_I for the s_{+-} pairing symmetry $\Delta_{uv\mathbf{k}} = \frac{1}{2}\Delta_0(\cos k_x + \cos k_y)$ with $\Delta_0 = 5.8$ meV at optimal electron doping ($\mu = -0.54$), where there are two Fermi surface sheets around Γ point.

increasing t or Δ_I , the single resonance splits into two peaks at symmetric energies. The resonance peak at positive energy has higher height than that at negative energy. It is interesting that the curves of the LDOS in Fig. 3(a) are same with those in Fig. 3(b) if t and Δ_I are replaced each other. In other words, t and Δ_I play the same role for the LDOS at the NN Fe sites of the IFI. This is the result that the Cooper pairs in the Fe-Fe plane tunnel through the IFI. We note that when $t = \Delta_I$, there is always a ZBS. If $t = \Delta_I$ is large, a strong resonance peak shows up at positive bias voltages in Fig. 3(c). However, for $t \gg \Delta_I$, the in-gap resonances move outside of the superconducting energy gap (see Fig. 3(d)).

In order to understand the variation of the in-gap bound states with the doping, we plot the LDOS curves near the IFI for the s_{+-} pairing symmetry under $\mu = 0.3$ and -0.45 , where there is no Fermi surface sheet and one Fermi surface sheet around Γ point, respectively, in Fig. 4. Obviously, in both cases, the LDOS at the IFI in Fig. 4(a) and (b) has a sharp zero energy resonance, and the superconducting coherence peaks are completely suppressed when $t = \Delta_I$. Meanwhile, there is only a ZBS at the NN Fe sites of the IFI in Fig. 4(c) and (d). The larger the parameter $t = \Delta_I$, the higher the zero energy resonance peak.

Now we investigate the low-lying electronic states induced by the IFI under different pairing symmetry in the bulk. In Fig. 5, we present the LDOS near the IFI at different physical parameters for the s_{++} pairing symmetry. After comparing Fig. 5 with Fig. 2(c), Fig. 3(c), and Fig. 4, we find that the LDOS curves for the s_{+-} pairing symmetry are identical with those for the s_{++} pairing symmetry in the presence of the same physical

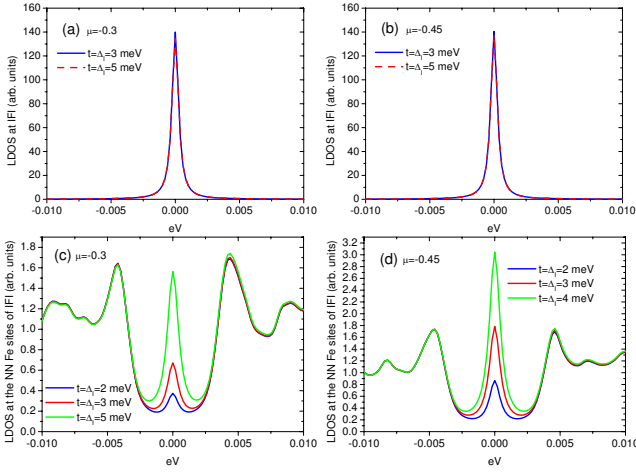


FIG. 4: (Color online) The LDOS at the IFI in (a) and (b) and the nearest neighboring Fe sites in (c) and (d) as a function of the bias voltage eV under $\mu = -0.3$, where there is no Fermi surface sheet around Γ point, and $\mu = -0.45$, where there is one Fermi surface sheet around Γ point, for the s_{+-} pairing symmetry $\Delta_{uv\mathbf{k}} = \frac{1}{2}\Delta_0(\cos k_x + \cos k_y)$ with $\Delta_0 = 5.8$ meV.

parameters. This means that the in-gap resonance peaks induced by the IFI is irrelative to the symmetry of the superconducting order parameter. Therefore, this out of the superconducting plane IFI is apparently different from the Zn impurity in cuprates [21,22] and the nonmagnetic impurity in the iron-based superconductors [18,24].

In summary, we have explored the impact of the IFI on the electronic states in the iron-based superconductors. This IFI is dealt as two electron channels with the orbital index α , which can also break the Cooper pairs when electrons tunnel through it. It is undoubted that re-forming new Cooper pairs with different magnitudes of the superconducting order parameter produces the in-gap resonances, which are determined by t and Δ_I and are independent of the pairing symmetry in the bulk. This implies that the resonance peaks induced by the IFI are not affected by a magnetic field. Obviously, the origin of these in-gap bound states is due to the Andreev reflection with the change of the magnitude rather than the phase of the superconducting order parameter, which is never reported in the superconductivity literature. We note that when both t and Δ_I are small, the LDOS near the IFI always has a single resonance peak at zero bias voltage, which is also irrelative to the doping. Such a robust ZBS is consistent with recent STM observations in the iron-based superconductor Fe(Te,Se) [23].

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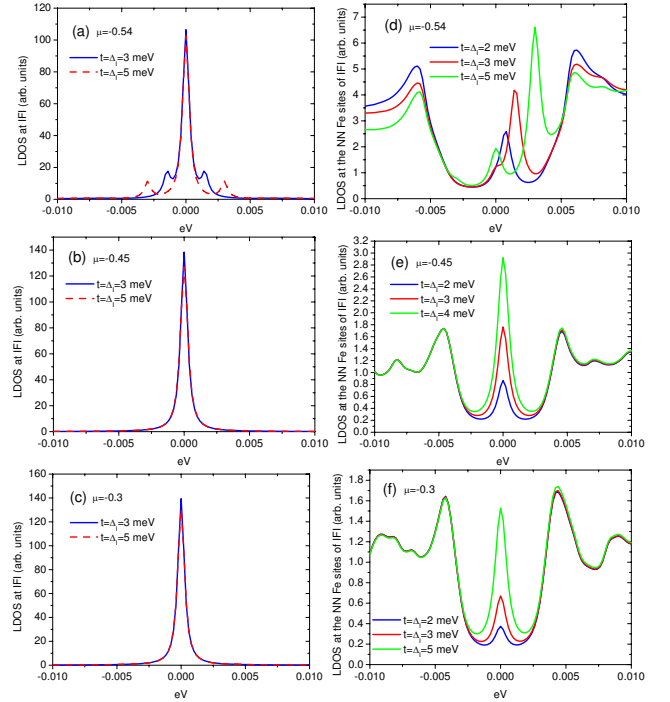


FIG. 5: (Color online) The LDOS at the IFI in (a)-(c) and the nearest neighboring Fe sites in (d)-(f) as a function of the bias voltage eV under different t and Δ_I for the s_{++} pairing symmetry $\Delta_{uv\mathbf{k}} = \frac{1}{2}\Delta_0|(\cos k_x + \cos k_y)|$ with $\Delta_0 = 5.8$ meV at different electron dopings.

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